An Approximate Determination of the Boiling Points of Metals.

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Despite the facility with which high temperatures can be reached and maintained constant by means of electric heating, no general investigation of the boiling points of the metals has yet been carried out, and such information as is available has in many cases been obtained by considerable extrapolation. Moreover, the published data are remarkably discordant, as will be seen from the individual results quoted below.

In the course of an extended experimental investigation, H. Moissan* has made observations on the vaporisation of metals at high temperatures by observing the loss of weight of a considerable mass of metal heated for definite periods of time in his arc furnace. O. P. Watts† has attempted to deduce from these experiments approximate values for the boiling points of the metals. In addition to the uncertainty due to the fact that many metals possess a high vapour tension at temperatures much below their actual boiling points, considerable errors are caused by the fact that Moissan does not appear to have measured the expenditure of energy in the furnace, which varies widely according to the conductivity of the vapours surrounding the arc. Also, in many of his experiments the temperature of ebullition must have been altogether modified by carburisation.

Since it is now possible to perform effectively the heating and to make relatively accurate temperature measurements in the region concerned, the remaining difficulty is largely due to our ignorance of any material capable of remaining gas-tight at sufficiently high temperatures.

For approximate measurements it has, however, been found possible to circumvent this difficulty and yet obtain a sufficiently definite proof that actual boiling is taking place.

In the present investigation the following metals have been studied: aluminium, antimony, bismuth, chromium, copper, iron, lead, magnesium, manganese, silver, tin.

Experimental Methods.

In some unpublished work carried out by Dr. L. Bradshaw in this laboratory, measurements were made of the loss in weight of a crucible,

* H. Moissan, 'Comptes Rendus,' vol. 142, p. 425 (1906).

† O. P. Watts, 'Trans. Amer. Electrochem. Soc.,' 1907, vol. 12, p. 141.

containing the metal under investigation, maintained for a definite time at constant temperature; it being hoped that, by repeating the measurements at fixed points over a wide range of temperature, the loss by volatilisation would enable a fairly close approximation of the boiling point to be deduced. It was found, however, that the volatilisation occurs over such a large temperature interval that in starting the present investigation other methods were resorted to.

In the first place thin-walled crucibles, containing a considerable amount of metal, were heated, either in a Moissan arc furnace* or in a carbon tube furnace, the energy consumption being kept constant and chosen so as to be capable of ensuring in the enclosure a temperature considerably higher than the boiling point of the metal under investigation.

During the heating the temperature of the outside wall of the crucible was measured at regular intervals by means of an optical pyrometer; it being anticipated that when the relatively large mass of metal entered into ebullition some definite indication would be obtained that the crucible walls ceased to show an increase in temperature. The measurements, however, were distinctly disappointing, the crucible walls rising considerably above the boiling point of the metal.

The method eventually adopted was to employ a vertical carbon tube resistance furnace,† in which was suspended a long graphite crucible which contained the metal under investigation (see fig. 1). The depth of metal employed was usually about 30 mm.‡ Temperature readings of the outer walls of the crucible were taken by means of a Wanner optical pyrometer, a side tube being provided exactly opposite the lower end of the crucible, and being so arranged that only the radiation from the crucible walls could fall on the pyrometer; the side tube was kept clear of vapours by a current of hydrogen.

The temperature of the heating tube, which could be readily raised to 2700°, was under delicate control by adjustment of the current passing through it.

The measurements of the boiling points were carried out by slowly raising the temperature of the crucible and observing the surface of the metal from above through an absorbing glass. At first the surface of the molten metal remains perfectly still, but as the boiling point is approached a slight agitation

* This method was employed by Féry ('Annales de Chimie et de Phys.,' sér. 7, vol. 28, p. 425). His values are 1040° C. for zinc and 2100° C. for copper.

† *Cf.* Hutton and Patterson, 'Trans. Faraday Soc.,' vol. 1, No. 2, p. 187.

‡ The tall crucible employed acts as a reflux condenser, so that the quantity of metal does not rapidly decrease. Moreover, comparative experiments proved that wide variations in the height of the metal had no influence on the boiling point indicated.

of the surface is observed which soon becomes vigorous. In the case of most of the metals studied, the difference between the temperature indicated when a gentle agitation is first apparent and that at which the ebullition has

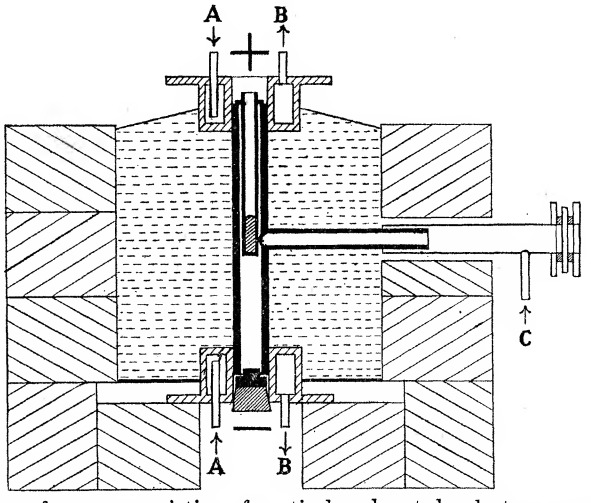

FIG. 1.—Resistance furnace, consisting of vertical carbon tube electro-coppered at the ends and soldered into brass castings, provided with water circulation at A and B. Temperature readings taken down the side tube of carbon, fixed into a brass tube with a window at the end, a current of hydrogen being admitted at C. The whole furnace was packed in crushed wood charcoal, while a thin walled graphite crucible contained the metal to be studied.

Scale 1 : 8.

become so violent that globules of metal are being ejected from the top of the tall crucible does not exceed 100°. By taking the boiling point as that temperature at which ebullition becomes decided, quite concordant results were obtained in different experiments, as will be seen from the detailed measurements in three experiments with silver, given below.

From the study of a large number of metals in this manner, it appears probable that the temperature at which the vaporisation becomes sufficiently rapid to cause a decided projection of drops from the surface may be taken with fair approximation as the boiling point; in the three experiments quoted this temperature is 1955°.

The question as to whether the temperatures measured on the outer surface of the crucible really indicate sufficiently accurately the actual temperatures of the metal is certainly an important one. Measurements made up to 1500° in comparison with a thermo-element indicate that the difference is not very great, but in order to obtain further confirmation and attempt to make use of a somewhat different method of measurement, an apparatus as shown in

I.				II.				III.			
Time from commencement.	Temperature.	Current amperes.		Time from commencement.	Temperature.	Current amperes.		Time from commencement.	Temperature.	Current amperes.	
mins.	°			mins.	°			mins.	°		
12	1800	320	Clear and still.	16	1770	260	Perfectly clear and still.	6	1440	330	Clear and still.
13	1820	320	,, ,,	18	1815	260	,, ,, ,,	9	1560	330	,, ,,
14	1860	320	Clear, gentle agitation at edges, centre still.	20	1860	260	,, ,, ,,	12	1670	360	,, ,,
15	1905	330	All surface in gentle agitation, no drops thrown up.	21	1875	290	Slight trace of movement at edges.	13	1730	360	,, ,,
				22	1880	290	Surface quiet.	16	1790	360	,, ,,
16	1915	330	,, ,, ,,	23	1915	290	Gentle agitation, no drops thrown up.	18	1840	370	,, ,,
17	1935	330	Drops thrown up very gently.	24	1925	290	,, ,, ,,	20	1860	370	Slight agitation at edges.
				25	1955	290	Decided agitation, drops thrown up gently.	21	1880	380	,, ,, ,,
18	1935	330	,, ,, ,,					22	1900	380	Clear, gentle agitation all over surface.
19	1955	330	Drops quite decided.					24	1920	380	Agitation decided, no drops thrown up.
20	1955	330	Drops thrown half way up crucible.	26	1955	300	,, ,, ,,				
				27	1975	300	Drops half way up crucible.	25	1935	390	Agitation decided, occasional drops.
21	1965	330	Drops sent out of crucible.	28	1975	300	Vigorous, drops projected out of crucible.	27	1955	390	Drops sent up decidedly.
22	1975	330	,, ,, ,,	29	1980	300	,, ,, ,,	29	1980	390	Drops vigorous, half way up crucible.
								30	2000	390	Drops projected out of crucible.

fig. 2 was employed. Here the heating is effected from the inside by a rod of carbon, an annular crucible containing the metal, and the temperature being read on the outer surface of the crucible as before; thus reversing the effect of errors in temperature measurement due to the thermal conductivity of the

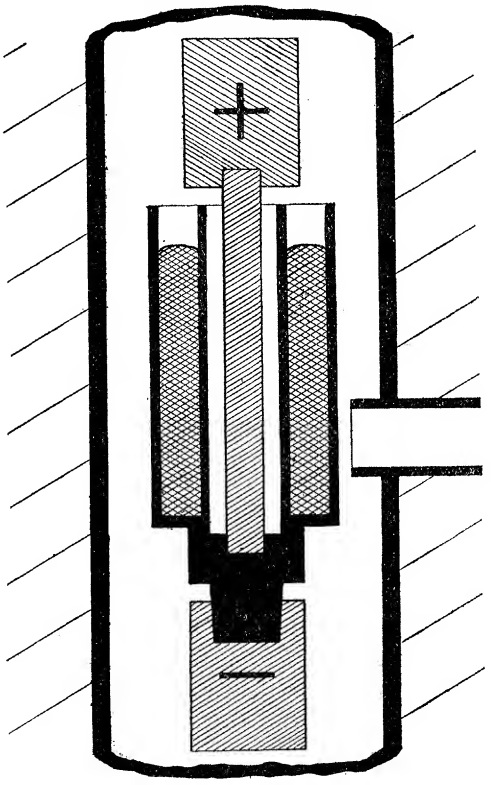

FIG. 2.—Annular crucible turned out of graphite, heating being effected electrically by means of the central carbon rod, which is supplied with current from the two thick graphite rods. The crucible is fixed inside a long wide carbon tube surrounded by Kieselguhr, and temperature readings taken through a side tube, just as with the apparatus shown in fig. 1.

Scale 2 : 5.

crucible walls, and altogether removing any possibility of reflexion of the radiation from the hotter surface of the heating tube.

Experiments made with lead proved a close agreement between the results obtained by the two methods, but all attempts to obtain limitation of the temperature of the outer wall whilst the metal was boiling, and when the heating rod was maintained at an excessively high temperature, proved abortive.

The current of hydrogen which was passed through the side tube of the

furnace (shown in fig. 1) was found to have quite a marked influence on the ebullition of the metal. If the current of hydrogen is stopped when the metal is gently boiling ebullition ceases. Moreover, when nitrogen was employed instead of hydrogen, the temperature readings were concordant in similar experiments, but were always considerably higher (50° to 100°) than those obtained in a hydrogen atmosphere.

This curious and unexpected effect appears to be due to the ease with which hydrogen permeates the crucible walls, removing and diluting the column of heavy vapour. If, after interrupting the admission of hydrogen for a brief period, the stream be restarted, it can be distinctly seen, on looking down the crucible, that the vapours above the metal surface are immediately dislodged by gas passing through the crucible walls. Using a slow current of nitrogen, on account of its much higher density, the values obtained are practically the same as if no gas at all were admitted.

A large number of measurements were made in a nitrogen atmosphere and the results are indicated below, but it seems probable that the values obtained with hydrogen approximate more closely to the boiling points of the metals at atmospheric pressure.

The use of a graphite crucible is naturally limited to such metals as do not appreciably combine with, or dissolve, carbon under the conditions of the experiment. As will be seen, modifications have to be introduced in the case of other metals.

Temperature Measurements.

Throughout this investigation the temperatures have been measured by a Wanner pyrometer sighted on the outer wall of the crucible containing the metal. This was made possible by the provision of a side tube as shown in fig. 1, the tube being kept free from vapours by a current of hydrogen.

In order to ensure the accuracy of the temperature readings, the current passing through the standard lamp of the pyrometer was carefully adjusted, an ammeter being included in the lamp circuit. Comparison with a thermo-element up to 1500° C. (using the correction for the difference between the optical and thermo-electric scales of temperature)* showed that the temperature scale provided with the instrument closely concorded with the measurements of the thermo-element.

In order, however, to render the results capable of subsequent correction, the pyrometer was standardised by measuring the "black body" temperatures of the melting points of platinum, rhodium, and iridium. These metals, which were specially prepared of a high degree of purity by

* *Cf.* Burgess, 'Trans. Amer. Electrochem. Soc.,' vol. 11, p. 247.

Messrs. Johnson, Matthey, and Co., were used in the form of strips 4 mm. wide by 8 cm. long, and were heated electrically, the pyrometer being sighted upon them.

The individual values, as measured with this pyrometer under identical conditions to the measurements for the boiling points, were as follows:—

Platinum.	Rhodium.	Iridium.
1545°	1670°	1995°
1560	1655	1985
1555	1680	2025
1545	1680	1990
—	1680	2035
Mean... 1551	1673	2006

Holborn and Henning* give the following "black body" values of the melting points:—platinum, 1545°; rhodium, 1650°; iridium, 2000°.

In view of the fact that such fixed points can readily be determined, and consequently the relative accuracy of the measurements given in the present work may be conveniently checked, it has been thought best to publish the results as they were obtained, without correction, it being clearly understood that the temperatures are all given on the optical scale.

The only correction introduced is a deduction of 20° from the values in the summary for temperatures below 1500°, as these were determined without any absorption glass before the pyrometer and standardisation under these conditions indicated this difference of 20°.

The main object of the investigation was to obtain approximate values for the boiling points measured under closely similar conditions, and thus clear away the uncertainty of the published data, which in several cases amounts to some hundreds of degrees. In order to obtain more accurate results, it remains to introduce refinements in the method which it was impossible to adopt in an attempt to extend the work over a large number of metals.

Copper.—Practically the only determination previously recorded of the boiling point of copper is that of Féry,† his value being 2100° C. Wartenberg,‡ from measurements of the vapour densities of the metals, and by observing at what temperatures they begin to assume the gaseous state rapidly, deduced approximate values for the boiling points of a few metals; he classes copper with tin and aluminium as probably above 2200° C.

* Sitzungsber. K. Akad. Wiss. Berlin,' 1905, vol. 12, p. 311.

† 'Annales de Chimie et de Physique,' sér. 7, vol. 28, p. 428 (1903).

‡ 'Z. für anorg. Chemie,' vol. 56, p. 320 (1908).

When measurements were made by the general method described above the different stages of the vaporisation were sharply indicated, a very clear surface of the metal being visible throughout.

The following results were obtained for electrolytic copper at intervals of several months, the atmosphere being hydrogen, which was admitted through the sighting tube for the pyrometer.

First gentle agitation of surface.	Decided ebullition.	Violent ejection of material from the crucible.
2250°	2300°	2350°
2300	2320	
2280	2320	2400
2230	2275	
2275	2320	2375

Boiling point. Mean approx. 2310°.

In nitrogen, as explained previously, the readings are considerably higher; the first agitation of the surface occurring at 2430°, decided ebullition at 2450°, and violent projection of material at 2475°.

An examination of the copper subsequent to the experiments indicated that a small amount of carbon had been dissolved, and, upon cooling, given up in the form of graphite.

Tin.—Carnelley and Williams* attempted to measure the boiling points of some metals by suspending above the surface of the highly heated metal small iron or fireclay tubes containing metals of known melting point; they record the boiling point of tin as between 1435° and 1505° C.,† and state that it boils very well and is more easily volatile than lead.

Wartenberg,‡ on the other hand, gives a probable value above 2200° C.

Moissan's experiments indicated that tin is less volatile than copper.

In the direct measurements made by the method described, the surface of the molten metal remained very clearly visible and the different stages were sharply indicated. The following values for tin were obtained in a hydrogen atmosphere.

In nitrogen the first general agitation of the surface occurs at 2220°, ebullition at 2350°, and violent projection of material at 2400°.

On subsequent examination, the metal did not appear to have been appreciably affected by the carbon.

* Carnelley and Williams, 'Journ. Chem. Soc.,' 1879, p. 563.

† M.P. of nickel and iron.

‡ *Loc. cit.*

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
2150°	2275°	2320°
2100	2250	2300
2150	2250	2300
2210	2295	2350
2200	2270	2340
2150	2270	2320
2170	2250	2300

Boiling point. Mean approx. 2270°.

Silver.—The value deduced by Wartenberg* from his vapour density determinations is 2070° C. With silver assaying 99·9 per cent. the following results were obtained in hydrogen, the readings being very concordant.

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1900°	1955°	1975°
1915	1955	1975
1915	1960	2000
1900	1955	2000

Boiling point. Mean approx. 1955°.

Silver is apparently very little affected by the carbon with which it was in contact at these high temperatures.

In nitrogen the first gentle agitation occurs at 2020°, ebullition at 2050° and projection of material at 2075°.

Lead.—Carnelley and Williams† give the boiling point as between 1435° and 1505° C., whilst Wartenberg estimated it at 1580° C.

With Merck's "extra pure" lead, the following direct determinations were made in a hydrogen atmosphere:—

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1475°	1520°	1585°
1475	1505	1540
1470	1540	1580
1475	1525	1600
1475	1525	1570

Boiling point. Mean approx. 1525°.

* *Loc. cit.* † *Loc. cit.*

In nitrogen the first gentle agitation of the surface commences at 1525°, boiling is distinctly visible at 1570°, and projection of material at 1600°.

Bismuth.—Carnelley and Williams found the boiling point to be between* 1084° and 1435° C., Barus,† by extrapolation from the values obtained at low pressure, gives as the approximate boiling point at atmospheric pressure 1550° C.

Using Merck's "extra pure" bismuth, the following readings were obtained in hydrogen, the surface of the metal being somewhat obscured above 1425° C. by the condensing metallic vapours. After the experiment the metal seems to be quite unchanged.

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1415°	1435°	1460°
1400	1425	1480
1420	1450	1500
—	1450	1500

Boiling point. Mean approx. 1440°.

In nitrogen the values deduced are 1450° for agitation of the surface 1500° for boiling point, and 1530° for violent boiling.

Antimony.—Several measurements have been recorded. Carnelley and Williams state that it lies between 1084° and 1435° C., Mensching and Meyer‡ above 1437° C., and Biltz and Meyer§ 1500° to 1700°.

Although the observation of the surface of the metal is in this case rendered somewhat difficult by the clouds of metallic vapour, the readings were fairly consistent.

The metal employed was Merck's "extra pure" antimony, and was apparently little affected by carbon after prolonged boiling.

First gentle agitation of the surface.	Decided ebullition.	Violent ejection of material from the crucible.
1420°	1455°	1500°
1400	1450	1470
1425	1470	1510
1425	1460	1505

Boiling point. Mean approx. 1460°.

In nitrogen the corresponding values were 1480°, 1530°, and 1570°.

* M.P. of copper and nickel.

† Barus, "Bull. U.S. Geolog. Survey, No. 103," 'Amer. Journl. Sci.,' (3), vol. 48, p. 332.

‡ Mensching and Meyer, 'Annalen,' vol. 240 (1887), p. 317.

§ Biltz and Meyer, 'Ber.,' 22, No. 1 (1889), p. 725.

Boiling Point Determinations of Metals which readily Carburise.

In these cases very great difficulties were encountered which for long made it impossible to obtain even roughly concordant results. Numerous attempts were made to apply the magnesia tubes of the Berlin porcelain factory as crucible materials, but even with very gradual heating they almost invariably cracked before the boiling point of the metal had been reached. Eventually, after further fruitless efforts with magnesia and thoria, a method was devised to "brasque" carbon crucibles with highly shrunk pure magnesia,* although still many of the experiments proved failures owing to the break-down of the lining. Only the results of these experiments in which the lining remained free from cracks, and in which none of the liquid metal had come in contact with the carbon, were considered suitable for the purpose in view. The graphite crucibles were 15 cm. long and 2·5 cm. internal diameter, a thick paste of the finely powdered magnesia, mixed with saturated magnesium chloride solution, was placed in the tube, and by means of a wooden former a uniform lining 2 mm. thick was obtained. After drying slowly at 200° C., the crucible was placed in the furnace, and the temperature gradually raised to about 1700° C., hydrogen chloride being given off copiously during the process. It was found that the minimum risk of the brasque cracking was secured by adding the charge of metal, after allowing the crucible only to cool to about 1300° C., the experiment being performed immediately afterwards. The magnesia brasques prepared in this manner remained perfectly hard and coherent after heating to 1800° C., and even when subjected to 2500° C. Some trouble is caused by the fact that at about 1700° C. the magnesia begins to react with carbon, giving a dark grey sublimate. This action is, however, not sufficiently vigorous to seriously interfere with the observation of the metal, except, perhaps, at the high ebullition temperature of iron.

Aluminium.—Deville stated that aluminium was not volatile at a white heat, and recently Wartenberg has estimated that the boiling point lies above 2200° C. In consideration of the facility with which this metal vaporises *in vacuo*, and also from observations on its behaviour in the electric furnace, it was suspected that this value was considerably too high.

In addition to its great affinity for carbon, another difficulty encountered with aluminium is the tenacious surface film of oxide which always covers the molten metal.

On gradually raising the temperature of the brasqued crucible with its

* Prepared by heating pure calcined magnesia, packed around a carbon rod maintained at a high temperature by passing through the rod an electric current.

charge of aluminium (about 3 cm. deep), there is no visible motion of the surface of the metal, and no marked sublimation until 1700° is reached. At 1790°, as read on the outside of the crucible, a sudden very vigorous agitation of the surface is observed: in some cases the metal frothed right up the crucible, and globules of metal were ejected very freely from the top of the crucible, a marked noise being also noticed.

To estimate the error due to the low thermal conductivity of the lining, the boiling points of silver and copper were determined under similar conditions in brasqued crucibles. The values obtained, however, were practically the same as those indicated above, so that no correction appears to be necessary. We may therefore fix the boiling point of aluminium as approximately 1800°. The metallic residue in the crucible, in all experiments which gave a definite indication of ebullition, was found to be only very slightly carburised.

How greatly carburisation affects the ebullition can be judged from the fact that aluminium heated in an unbrasqued graphite crucible to 2100° shows not the slightest sign of boiling.

Manganese.—The difficulties in this case were even greater than with aluminium, on account both of the higher temperature of vaporisation and of the marked corrosive action of the metal upon the magnesia brasque. Consequently only a few of the numerous experiments proved successful.

The metal employed was Merck's "extra pure" fused manganese, which was found to be free from aluminium. The different stages of the boiling were quite clearly defined owing to the absence of any surface film. A slight agitation of the surface was apparent at 1850°, ebullition at 1900°, and at 1950° the metal vapour was burning at the top of the crucible with a large yellowish flame.

The boiling point may be given approximately as 1900°.

In an unbrasqued crucible no marked vaporisation of the metal was obtained at 2200°, thus showing the great effect of carburisation.

First gentle agitation of surface.	Decided ebullition.	Very vigorous ebullition.
1850°	1875°	—
1850	1900	—
1860	1890	1925

Chromium.—In this case also the brasque is to some extent acted upon by the metal, but fairly definite observations could be made, showing the agitation of the surface to commence at about 2175° and boiling at about

2250°. In an unbrasqued crucible no marked volatilisation is observed at 2500°.

Magnesium.—Until recently the measurement of Ditte,* who found the boiling point to be 1100°, has not been seriously thrown in doubt, but Wartenberg's† published results group magnesium with copper, tin, and aluminium, with boiling point above 2200°. It is difficult to see to what this uncertainty is due. In a graphite crucible, steady ebullition is clearly visible at 1100°, and measurements made with a protected thermo-element immersed in the molten metal indicate a well defined constancy of temperature for some minutes about 1120°, the metal distilling off. There seems little reason, therefore, for classing magnesium with metals of high boiling point.

Iron.—With iron of 99·9 per cent. purity, ebullition was found to set in at about 2450°. Observations of the surface were rendered difficult by the products of the reaction between the magnesia and carbon, which at this high temperature is very vigorous. The carbon content of the metal after the experiments was under 0·1 per cent.

Conclusion.

Subject to the corrections which may be necessary when the temperature scale has been more accurately fixed, the following approximate measurements may be given of the boiling points as determined in the present investigation :—

Aluminium	1800°	Lead	1525°
Antimony	1440	Magnesium	1120
Bismuth	1420	Manganese	1900
Chromium	2200	Silver	1955
Copper	2310	Tin	2270
Iron	2450		

Some of the incidental expenses of this research have been borne out of the funds provided by the Government Grant Committee of the Royal Society. I wish to express my indebtedness to Dr. R. S. Hutton for his continual interest and advice during the progress of the work.

* 'Comptes Rendus,' vol. 73 (1871), p. 108.

† *Loc. cit.*